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INCREASING REINFORCING GLASS FABRIC IMPREGNABILITY BY USING ADHESIVES

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The possibility of increasing the anhydride epoxy bonding agent impregnability of glass fabric, made from aluminum borosilicate glass, by introducing adhesives into the serially produced lubricant 4s is studied. A wide range of wetting agents, produced by different global manufacturers for fiber and organosilicon coupling agents, was tested by determining the bonding agent impregnability over the height in a capillary. The impregnability of reinforcing glass fabric was increased considerably by improving the lubricant as well as counter-modification of the bonding agent.

Key words: fiberglass, wetting agent, silane, lubricant, impregnability, bonding agent.

The performance of glass reinforced plastics depends on the physical-chemical characteristics of the initial components — polymer and reinforcing material — and their ratio and integration quality in the composition [1]. The interaction of the components at the polymer – reinforcing filler interface plays an important role.

Increasing the strength of fiberglass is a very important problem. This can be accomplished by, among other things, increasing the polymer impregnability of the lubricant-treated fiberglass.

The objective of the present work is to evaluate the effectiveness of wetting agents introduced into the lubricant to increase the impregnability of fiberglass treated with an anhydride epoxy bonding agent and its modifications.

The wetting agents, developed by different global producers for fiber material, deposited on 7628/12-71-TO glass fabric made of type E aluminum-borosilicate glass, was studied by determining the polymer composition impregnability of fiber materials over the rise height of the bonding agent in a capillary.

The data obtained show that 1% water solutions of the following commercial wetting agents impart high impregnability to pure aluminum-borosilicate fiberglass: Nioksol NS-SM (NPO PAVTEK, JSC), Sintamid-5K (Sintez OKA, JSC), Neonol 9-6, Neonol 9-10 (Nizhnekamskneftekhim, JSC), Sintanol-7 (Zavod Sintanolov, JSC), BYK-W 996, BYK-W 9010 (BYK Chemie), Silwet L-77, L-7210, Coatosil 1220, LE-743 (Momentive), Q2-5211 (Dow Corning GmbH), Sandoclean PCJ (Clariant), Tween-81 (Americas, Ins. Atlas Point).

In industry, all continuous glass fibers are coated by lubricants at the output [2].The composition of the lubricant has a very large effect on the quality of the glass fiber and composite based on it. Today, in glass fiber production the most promising lubricant for obtaining epoxy fiberglass is the lubricant 4s.

In the present work, the effectiveness of wetting agents as additives to the lubricant 4s in concentrations guaranteeing the stability of the experimental variants of wetting agents during three-day storage (the technology using silane lubricants for glass fiber permits using freshly prepared composition within 3 days). The 4s compositions based lubricants improved by wetting agents are presented in Table 1.

The impregnability data show convincingly that the glass fibers treated with the following modifications of the lubricant 4s possess the best impregnability by anhydride epoxy bonding agent: non-fluorinated organo modified siloxane surfactant Coatosil 1220 (see Table 1, composition c), synergetic mixture of alkyl ethoxylates and fatty alcohols Sandoclean PCJ (Table 1, composition m), siloxane copolymer polyalkyleneoxide Silwet L-7210 (Table 1, composition i), mixture of non-ionic surfactants Nioksol NS-SM (Table 1, composition g), sorbitan derivative mono-9-octadecanoate poly(oxy-1,2-ethanediol) Tween-81 (Table 1, composition j) (Fig. 1).

It was determined that the introduction of the lubricants mentioned above into the serially produced lubricant 4s considerably increases the rate of permeation during the first

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TABLE 1. Compositions of Wetting Agent Improved Lubricants Based on the Serially Produced Lubricant 4s

Lubricant compositions*	Composition
4s + 0.2% Sintanol-7	a
4s + 0.6% BYK-W 9010	b
4s + 0.1% Coatosil 1220	c
4s + 0.2% Neonol 9-6	d
4s + 1.0% BYK-W 996	e
4ñ +0.2% Neonol 9-10	f
4s + 0.3% Nioksol NS-SM	g
4s + 0.1% LE-743	h
4s + 0.1% Silwet L-7210	i
4s + 0.2% Tween-81	j
4s + 0.1% Q2-5211	k
4s + 0.1% Silwet L-77	l
4s + 0.2% Sandoclean PCJ	m
4s + 0.2% Sintamid-5K	n

* Content, wt.%

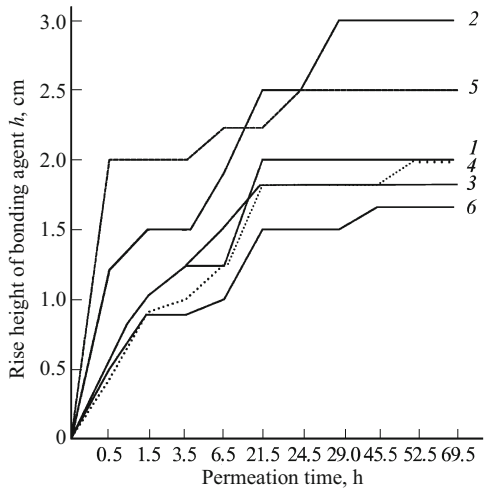

Fig. 1. Anhydride epoxy permeation of glass fabric treated with modifications of lubricant 4s with wetting agents: *1*) 4s + Nioksol NS-SM; *2*) 4s + Coatsil 1220; *3*) 4s + Tween-81; *4*) 4s + Silwet L-7210; *5*) 4s + Sandoclean PCJ; *6*) 4s.

hour. This indicator is very important for the formation of fiberglass by high-velocity pultrusion.

The introduction of the other tested wetting agents into the lubricant 4s (Table 1, compositions a, b, d, e, f, h, k, l, n) degrades the impregnability of the glass fibers treated with anhydride epoxy compared with the lubricant 4s.

Maximum impregnability is reached in one day from the start of the experiment for practically all wetting agents.

Because of their functional groups organosilicon coupling agents (silanes) interact chemically with the surface groups of a glass fiber. Silanes deliver organic groups to the surface and, first and foremost, improve fiber wettability by a polymer bonding agent [3]. For this reason, in the present work they too were studied as wetting agents.

Silanes produced by the leading global manufacturers and recommended for epoxy bonding agents were studied. They possess the following functional groups: γ-amino-, γ-glycidoxy-, γ-methacryloxy-, γ-ureido- and the newest polyfunctional silanes [4].

The following coupling agents were studied in the present work:

1) A-1100 (Momentive) — γ-aminopropyltriethoxysilane;

2) A-1120 (Momentive) — N(ß-aminoethyl)-γ-aminopropyltrimethoxysilane;

3) A-174 (Momentive) — γ-methacryloxypropyltrimethoxysilane;

4) A-187 (Momentive) — γ-glycidoxypropyltrimethoxysilane;

5) VS-142 (Momentive) — water solution of A-1100 in perhydrolized form;

6) A-1387 (Momentive) — siliconized silane polyazamide;

7) A-1524 (Momentive) — γ-ureidopropyltrimethoxysilane;

8) Z-6032 (Dow Corning) — N(ß-aminoethyldivinylbenzene)-γ-aminopropylvinylbenzyltrimethoxysilane.

All silane brands 1, 2, 4, 5 and 6 dissolve well in water, samples 3 and 7 dissolve with intense mixing, and silane 8 self-disperses with a white emulsion being formed.

Since lubricating compositions must be uniform and stable in storage for at least three days, the compatibility of the silanes chosen as well as mixtures of silanes with lubricant 4s were studied.

The 4s-based lubricant compositions for testing are presented in Table 2. It should be noted that the serially produced lubricant 4s contains 5% organosilicon coupling agent A-1100.

It was determined from the data on the anhydride epoxy impregnability of glass fabric treated with lubricant 4s together with silanes that fiberglass treated with modifications of lubricants which are a serial composition of the lubricant 4s with the addition of Z-6032 (see Table 2, composition 3s14) and A-1387 silane polyazamide (see Table 2, composition 4s10) exhibit the highest anhydride epoxy bonding agent impregnability. The composition 4s + 0.2% Z-6032 exhibited the best impregnability compared with all lubricant samples. However, it should be noted that N(ß-aminoethyldivinylbenzyl)-γ-aminopropylvinylbenzyltrimethoxysilane Z-6032, which was introduced into the lubricant 4s with no aminosilane A-1100, showed the lowest impregnability. Silane polyazamide A-1387 also exhibits similar behavior.

Replacing the aminosilane A-1100 with γ-glycidoxypropyltrimethoxysilane A-187 and γ-ureidopropyltrimethoxysilane A-1524 in the standard lubricant 4s in equal concentrations improves the impregnability of treated fiberglass.

The addition of γ-methacryloxypropyltrimethoxysilane A-174 to the serial composition 4s increases the anhydride epoxy bonding agent impregnability.

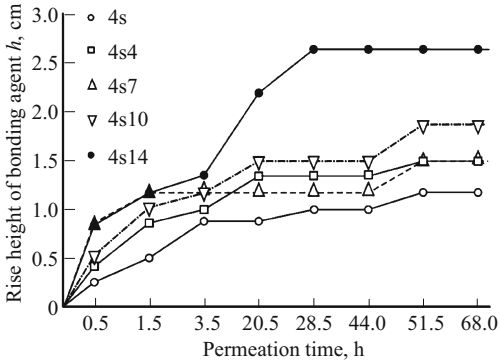

Fig. 2. Anhydride epoxy bonding agent permeation of fiberglass treated with the best lubricants (see Table 2) with addition of silane (t = 24°C).

Increasing the mass fraction of γ-aminopropyltriethoxysilane A-1100 in the standard 4s lubricant degrades the wetting properties. In addition, increasing the concentration of aminosilane A-1100 from 0.5 to 0.8% significantly decreases the impregnability of treated glass fibers. Increasing the aminosilane A-1100 content to 1.0% increases impregnability very little, but only to the level of the impregnability attained with the 4s prescription, where the A-1100 content is two times lower. Since aminosilane is the most expensive component of the lubricant, it is best to secure the required technological level of the properties of fiberglass with minimal concentrations of this product.

N(ß-Aminoethyl)-γ-aminopropyltrimethoxysilane A-1120 is an organosilicon coupling agent, containing primary and secondary amino groups in its molecular structure. Experiments have shown convincingly that the secondary amino group in the formula for silane impedes impregnability of fiberglass treated with anhydride epoxy bonding agent.

Lowering the A-1100 aminosilane mass fraction to 0.3% and adding 0.3% γ-glycidoxypropyltrimethoxysilane A-187 degrades the anhydride epoxy bonding agent impregnability of fiberglass.

Lowering the γ-aminopropyltriethoxysilane concentration to 0.1%, increasing the γ-methacryloxypropyltrimethoxysilane A-174 to 0.6% and adding 0.4% γ-glycidoxypropyl-trimethoxysilane A-187 lowers the anhydride epoxy impregnability of treated fiberglass.

It was determined that practically all combinations of the organosilicon coupling agents tested increase the rise height of the bonding agent in a capillary during the first 30 min of the experiment compared with the serial prescription 4s.

The serial lubricant modifications 4s + 0.2% N(ß-aminoethyldivinylbenzyl)-γ-aminopropylvinylbenzyltrimethoxysilane Z-6032 and 4s (no 0.5% A-1100) + 0.5% γ-ureidopropylmethoxysilane A-1524 have the highest initial permeation rate.

It was determined that fiberglass treated with 4s-lubricant modifications with addition of 0.2% N(ß-amino-ethyldivinylbenzyl)-γ-aminopropylvinylbenzyltrimethoxysilane Z-6032 and silane polyazamide A-1387 has the highest anhydride epoxy bonding agent impregnability (Fig. 2).

TABLE 2. 4s-Based Lubricant with Silanes

Composition	Lubricant composition
4s1	4s + 0.3% A-1100
4s2	4s + 0.5% A-1100
4s3	4s (no 0.5% A-1100) + 0.5% A-1120
4s4	4s (no 0.5% A-1100) + 0.5% A-187
4s5	4s (no 0.5% A-1100) + 1.0% VS-142
4s6	4s (no 0.5% A-1100) + 0.5% A-1387
4s7	4s (no 0.5% A-1100) + 0.5% A-1524
4s8	4s + 0.2% A-1524
4s9	4s (no 0.5% A-1100) + 0.5% Z-6032
4s10	4s + 0.2% A-1387
4s11	4s + 0.4% A-174
4s12	4s (no 0.4% A-1100) + 0.6% A-174 + 0.4% A-187
4s13	4s (no 0.2% A-1100) + 0.3% A-187
4s14	4s + 0.2% Z-6032

The possibility of improving the permeation of fiberglass treated with the lubricant compositions 4s + 0.2% Z-6032 and 4s + 0.2% A-1387 by introducing wetting agents into them is also of interest (Table 3).

The impregnability was improved by introducing the wetting agents Sandoclean PCJ, Coatsil 1220, Silwet L-77, BYK-W 9010 (see Table 3, compositions B, C, D and E).

The data on the impregnability by the improved lubrication compositions are presented in Fig. 3.

The system 4s + 0.2% A-1387 with added 0.1% Coatosil 1220, 0.1% Silwet L-77 and 0.66% BYK-W 9010 (the compositions J, K and L, respectively) exhibited the highest degree of permeation. These wetting agents, introduced into the system 4s + 0.2% Z-6032 (the compositions C, D and E), de-

TABLE 3. Compositions of Improved 4s-Based Lubricants with Wetting Agents Added

Composition	Composition of improved lubricant
A	4s + 0.2% Z 6032 + 0.3% Nioksol NS-SM
B	4s + 0.2% Z 6032 + 0.2% Sandoclean PCJ
C	4s + 0.2% Z 6032 + 0.1% Coatosil 1220
D	4s + 0.2% Z 6032 + 0.1% Silwet L-77
E	4s + 0.2% Z 6032 + 0.6% BYK-W 9010
F	4s + 0.2% Z 6032 + 1.0% BYK-W 996
G	4s + 0.2% Z 6032 + 0.5% Sintamid-5K
H	4s + 0.2% A-1387 + 0.3% Nioksol NS-SM
I	4s + 0.2% A-1387 + 0.2% Sandoclean PCJ
J	4s + 0.2% A-1387 + 0.1% Coatosil 1220
K	4s + 0.2% A-1387 + 0.1% Silwet L-77
L	4s + 0.2% A-1387 + 0.6% BYK-W 9010
M	4s + 0.2% A-1387 + 1.0% BYK-W 996
N	4s + 0.2% A-1387 + 0.5% Sintamid-5K

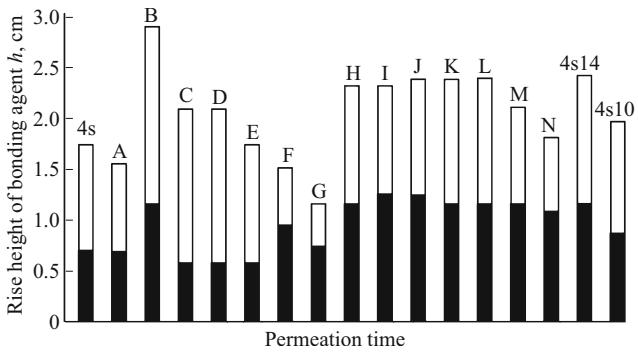

Fig. 3. Anhydride epoxy permeation of fiberglass treated with systems based on the best lubricants with the addition of silanes (see Table 2) together with the best wetting agents (see Table 3) (t = 18 °C): ■) permeation time 0.5 h; □) permeation time 29.0 h.

grade the impregnability of epoxy anhydride bonding agent treated fiberglass.

Adding the wetting agent Nioksol NS-SM to the system 4s + 0.2% A-1387 (composition H) increases the impregnability but only to the level of 4s + 0.2% Z-6032 (composition 4s14). This wetting agent, introduced into the system 4s + 0.2% Z-6032 (composition A), decreases the impregnability even compared with the pure lubricant 4s.

The wetting agents BYK-W 996 and Sintamid-5, added to the lubricants 4s + 0.2% A-1387 (compositions M and N, respectively), showed good impregnability by epoxy anhydride bonding agent treated fiberglass compared with the system 4s + 0.2% A-1387 (composition 4s10) but lower than the level of the lubricant 4s + Z-6032 (composition 4s14).

Adding the wetting agents BYK-W 996 and Sintamid-5K to the lubricant 4s + Z-6032 revealed the lowest impregnability (the compositions F and G, respectively).

The following systems possess the highest permeation rate: 4s + 0.2% Z-6032 + 0.2% Sandoclean PCJ; 4s + 0.2% A-1387 + 0.3% Nioksol NS-SM; 4s + 0.2% A-1387 + 0.2% Sandoclean PCJ; 4s + 0.2% A-1387 + 0.1% Coatosil 1220; 4s + 0.2% A-1387 + 0.1% Silwet L-77; 4s + 0.2% A-1387 + 0.6% BYK-W 9010; 4s + 0.2% A-1387 + 1.0% BYK-W 996.

Tested brands include the following wetting agents: BYK-A 500, BYK-A 515, BYK-A 525, BYK-A 530, BYK-410, BYK-W 995 and BYK-W 940. They do not dissolve or partially dissolve in water, i.e., they cannot be introduced into a water composition of the lubricant 4s. They dissolve well in ÉD-20 resin, which is a constituent of anhydride epoxy bonding agent (ÉAS). For this reason, in order to determine the wetting capacity of these wetting agents they were introduced into the bonding agent, which was allowed

TABLE 4. Permeation of Glass Fabric Treated with Modified Bonding Agents (t = 18°C)

Lubricant on fiberglass	Bonding agent	Rise height of bonding agent h, cm, with glass fabric treatment time, h						
		0.5	1.5	3.5	5.5	22.0	25.5	29.2
4s	ÉAS + BYK-A 500	1.2	1.5	1.5	1.8	2.0	2.0	2.0
4s	ÉAS + BYK-A 515	0.5	0.8	1.0	1.0	1.3	1.5	1.5
4s	ÉAS + BYK-A 525	0.6	0.8	1.0	1.0	1.3	1.3	1.3
4s	ÉAS + BYK-A 530	1.0	1.5	1.5	1.5	2.0	2.0	2.0
4s	ÉAS + BYK-410	0.5	0.7	1.0	1.0	1.3	1.4	1.4
4s	ÉAS + BYK-W 940	0.7	1.1	1.1	1.2	1.3	1.3	1.3
4s	ÉAS + BYK-W 995	0.5	1.0	1.2	1.4	1.8	2.0	2.0
4s + Z6032	ÉAS + BYK-A 500	1.0	1.5	1.8	1.8	2.0	2.0	2.0
4s + Z6032	ÉAS + BYK-A 515	0.8	1.2	1.4	1.6	1.8	2.0	2.0
4s + Z6032	ÉAS + BYK-A 525	0.6	1.0	1.2	1.5	2.0	2.0	2.0
4s + Z6032	ÉAS + BYK-A 530	1.2	1.6	1.8	2.0	2.3	2.3	2.3
4s + Z6032	ÉAS + BYK-410	0.5	1.0	1.2	1.5	2.0	2.0	2.0
4s + Z6032	ÉAS + BYK-W 940	0.7	1.2	1.2	1.4	1.8	2.0	2.0
4s + Z6032	ÉAS + BYK-W 995	1.0	1.2	1.4	1.6	2.0	2.0	2.0
4s + Z6032 + Sandoclean PCJ	ÉAS + BYK-A 500	1.2	1.5	1.7	2.0	2.0	2.2	2.2
4s + Z6032 + Sandoclean PCJ	ÉAS + BYK-A 515	0.6	1.4	1.4	1.5	1.6	2.1	2.1
4s + Z6032 + Sandoclean PCJ	ÉAS + BYK-A 525	1.0	1.0	1.1	1.2	1.8	2.0	2.0
4s + Z6032 + Sandoclean PCJ	ÉAS + BYK-A 530	1.7	2.2	2.4	2.5	3.2	3.5	3.5
4s + Z6032 + Sandoclean PCJ	ÉAS + BYK-410	0.7	1.0	1.0	1.2	1.6	2.5	2.5
4s + Z6032 + Sandoclean PCJ	ÉAS + BYK-W 940	0.7	1.6	1.6	1.6	1.6	1.6	1.6
4s + Z6032 + Sandoclean PCJ	ÉAS + BYK-W 995	1.0	1.0	1.2	1.5	1.8	2.5	2.5
4s	ÉAS	0.8	1.2	1.3	2.0	2.0	2.0	2.0
4s + Z6032	ÉAS	1.0	1.5	1.8	2.0	2.3	2.5	2.5
4s + Z6032 + Sandoclean PCJ	ÉAS	1.3	1.8	2.0	2.2	2.6	2.8	2.8

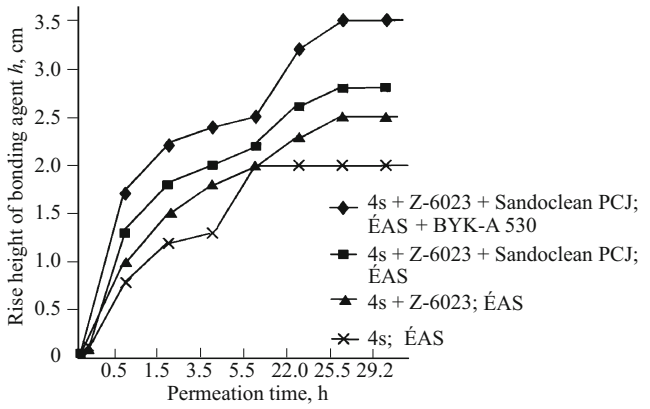

Fig. 4. Anhydride epoxy bonding agent permeation of fiberglass treated with the best lubricants (t = 18°C).

to permeate fiberglass treated with experimental variants of the lubricants.

The impregnability data are presented in Table 4.

The modification of ÉAS with the addition of 1.0% BYK-A 530 possesses the highest impregnability of fiberglass treated with the composition 4s + 0.2% Z-6032 + 0.2% Sandoclean PCJ. This system behaved worse than pure ÉAS on fiberglass treated with the lubricant 4s + 0.2% Z-6032.

Adding1.0% BYK-A 530 to anhydride epoxy bonding agent increases the impregnability of fiberglass treated with pure lubricant 4s.

Pure anhydride epoxy bonding agent exhibits high impregnability of fiberglass treated with 4s + 0.2% Z-6032 + 0.2% Sandoclean PCJ. Adding to ÉAS the wetting agents BYK-410, BYK-W 995, BYK-A 500, BYK-A 515, BYK-A 525 and BYK-W 940 interferes with the impregnation of fiberglass treated with the system 4s + 0.2% Z-6023 + 0.2% Sandoclean PCJ.

Fiberglass treated with the lubricant 4s + 0.2% Z-6032 is permeated best by pure ÉAS. Introducing BYK-A 530, BYK-410, BYK-W 995, BYK-A 500, BYK-A 515, BYK-A 525 and BYK-W 940 decreases impregnability.

Adding to anhydride epoxy bonding agent the wetting agents BYK-A 500 and BYK-A 530 increases the impregnability of fiberglass treated with pure lubricant 4s, but the increase is smaller than for permeation of pure ÉAS into fiberglass treated with the compositions 4s + 0.2% Z-6023 + 0.2% Sandoclean PCJ and4s + 0.2% Z-6032. Adding to ÉAS the wetting agent BYK-W 996 does not change the impregnability of fiberglass treated with the lubricant 4s on the pure bonding agent. The wetting agents BYK-A 515, BYK-410, BYK-W 940 and BYK-A 525 added to ÉAS decrease impregnability.

The following systems exhibit the highest initial permeation rate:

– 4s + 0.2% Z-6032 on the bonding agent ÉAS + 0.5% BYK-A 500;

– 4s + 0.2% Z-6032 on the bonding agent ÉAS + 0.5% BYK-A 530;

– 4s + 0.2% Z-6032 + 0.2% Sandoclean PCJ on the bonding agent ÉAS + 0.5% BYK-A 500;

– 4s + 0.2% Z-6032 + 0.2% Sandoclean PCJ on the bonding agent ÉAS + 0.5% BYK-A 530;

– 4s + 0.2% Z-6032 + Sandoclean PCJ on the bonding agent ÉAS + 1.0% BYK-W 995;

– 4s + 0.2% Z-6032 on the bonding agent ÉAS;

– 4s + 0.2% Z-6032 + Sandoclean PCJ on the bonding agent ÉAS.

This research shows that when organosilicon coupling agents are added as wetting agents fiberglass treated with the lubricant 4s + 0.2% Z-6032 wetting agent has the highest anhydride epoxy bonding agent impregnability.

When fabric is impregnated by lubricants based on the best lubricant compositions of silanes together with the best wetting agents the system 4s + 0.2% wetting agent Z-6032 + 0.2% Sandoclean PCJ (mixtures of alkylethoxylated and fatty alcohols) exhibits the highest initial permeation rate.

When glass fabric is impregnated with the improved compositions of the bonding agent the composition 4s + 0.2% wetting agent Z-6302 + 0.2% Sandoclean PCJ on anhydride epoxy bonding agent + 1.0% BYK-A 530 siloxane polymer solution exhibits the highest impregnability.

The composition 4s + 0.2% Z-6032 + 0.2% Sandoclean PCJ on anhydride epoxy bonding agent + 1.0% BYK-A 530 exhibits the highest initial permeation rate among the improved lubricant compositions.

In summary, the experiments lead to the development of the composition 4s + 0.2% Z-6023 + 0.2% Sandoclean PCJ (on anhydride epoxy bonding agent) + 1.0% BYK-A 530 with a high initial permeation rate, which also significantly increases the anhydride epoxy bonding agent impregnability of fiberglass made of E-type aluminum-borosilicate glass (Fig. 4).

These experiments prove convincingly that wetting agents based on a synergetic mixture of alkylethoxylated fatty alcohols Sandoclean PCJ (Clariant Company), nonfluoridated organo modified siloxane surfactant Coatosil 1220 (Momentive Company), as well as silanes N(ß-aminoethyldivinylbenzyl)-γ-aminopropylvinylbenzyltrimethoxysilane Z-6032 (Dow-Corning Company), and silane polyazamide A-1387 (Momentive Company) introduced into lubricant 4s, greatly increase the anhydride epoxy bonding agent impregnability of fiber made of E-type glass.

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